Effect of Sorbed Oil on Food Aroma Loss through Packaging Materials

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Mass transport of six food aroma components, D-limonene, *n*-decane, ethyl caproate, phenylethanol, 1-hexanol, and hexanal, through three sealable polymer films suitable for direct food contact, ultra-low-density polyethylene (ULDPE), ionomer (ION), and modified polyester (mPET), was analyzed by permeation experiments. Transport was characterized by the permeability coefficient and its two contributing factors, the diffusion coefficient (related to kinetics) and the solubility coefficient (related to equilibrium). The results show that ULDPE is more permeable to aromas that ION, which is more so than mPET. Differences in diffusivity are mainly responsible for barrier improvement. With aromas, nonpolar compounds permeate faster than polar ones through ULDPE. The effect of sorbed oil on the behavior of these materials as food aroma barriers was investigated. The sorption of oil apparently resulted in polymer swelling, increasing the solubility of aromas into the polymer matrixes. Little or no effect was found on the values of the diffusion coefficient. The permeability coefficient was affected as a consequence of changes in solubility. When aromas were compared, the transport of nonpolar penetrants showed a considerable increase while permeability values for the polar ones were either unaffected or even reduced. This behavior has been discussed in terms of polymer/oil/aroma compatibility.

Keywords: *Permeation; aromas; thermosealable polymers; sorbed oil*

INTRODUCTION

Due to their flexibility, variability in size and shape, thermal stability, and barrier properties, plastics are extensively used in packaging. Their use either alone or in combination with other materials has grown dramatically. In food packaging, they have not only substituted other materials but also expanded together with food product development into specialties such as snacks, baby formulas, pet foods, microwavable foods, and products requiring aseptic or modified atmosphere packaging.

One of the most important limitations of plastic packaging is that polymers allow the mass transport of low molecular weight substances (permeation, migration, and sorption). Through the measurement and understanding of mass transport, packages are designed to control this phenomenon during the shelf life of the product. However, the packaging of fatty foodstuffs is often problematic.

It is known that when large amounts of substances are sorbed in a polymer, its structure may be plasticized, affecting many of its properties (Brody and Marsh, 1997). Plasticization is a known modification of polymeric materials. Thus, some packaging materials such as flexible poly(vinyl chloride) incorporate plasticizers to reduce their rigidity. These substances act by decreasing the intercatenary forces which cause macromolecular cohesion. As well as modifying flexibility, many other properties of the polymer are affected: reduction of fragility, greater elongation at break,

reduction of the glass transition temperature, increase in permeability, etc. However, plasticization can also be induced as a result of undesirable mass transport. Hydrophilic materials such as polyamides or ethylene–vinyl alcohol copolymers are plasticized by water (Hernandez and Gavara, 1994; Gavara and Hernandez, 1994). Similarly, nonpolar solvents plasticize hydrophobic materials. Oxygen permeability through polyethylene has been shown to be increased by vegetable oil sorption and limonene sorption (Johansson and Leufven, 1994; Sadler and Braddock, 1990).

Polyethylenes (PEs) are the most common plastics used in packaging manufacture, either alone or as the innermost layer of packaging structures; in either case it is the material in direct contact with the contents (Catala and Gavara, 1996). PE is a hydrocarbon with hydrophobic and lipophilic characteristics. It provides a good water barrier as well as the necessary thermal sealability to make a hermetic container. However, its lipophilicity may be inconvenient for the packaging of products containing nonpolar substances such as fats, oils, or aromas, as these may be sorbed into the polymer or permeate through it.

In a previous paper (Hernandez-Muñoz et al., 1998), we reviewed the most significant studies on aroma scalping by polyolefins. Aroma components are normally present in foods at low levels, and their loss affects organoleptic properties but hardly affects the package. Oils and fats, which are the main constituents of many foodstuffs, are other nonpolar compounds capable of diffusing through plastics. In contrast to flavors, the sorption of fats does not significantly alter product quality since the quantity sorbed is negligible compared with total content. However, the effect on the package

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may well be quite important. This may be the case for polyethylenes. The sorption of large amounts of oil may affect barrier properties and increase the already high aroma permeability.

There are some materials that can substitute PEs in package design for fatty foodstuffs. Ionomers are PE-based copolymers with ion groups which are claimed to reduce fatty food/packaging interactions. Polyester is an outstanding polymer material which has been recently modified to allow package sealability. In this paper, we compare three sealable plastic films, an ultra-low-density polyethylene (ULDPE), an ionomer (ION), and a modified polyester (mPET), suitable for food contact. The aim was to check their performance as aroma barriers on contact with aromatic fatty foodstuffs, such as cured meats. Mass transport is characterized through the evaluation of the permeability (P), diffusion (D), and solubility (S) coefficients. The effect of oil sorption on barrier properties is also determined and discussed through P, D, and S values.

MATERIALS AND METHODS

Three thermosealable films, an ultra-low-density polyethylene, ULDPE (Attane 4002, Dow Chemical, Midland, MI), a sodium ionomer, ION (Surlin 1605, DuPont Ibérica, Barcelona, Spain), and a modified poly(ethylene terephthalate), mPET (Selar PT, DuPont de Nemours, Wilmington, DE), were the subject of study. Their respective thicknesses, measured in a micrometer (Metrotec, San Sebastian, Spain) were 45, 60, and 30 μm.

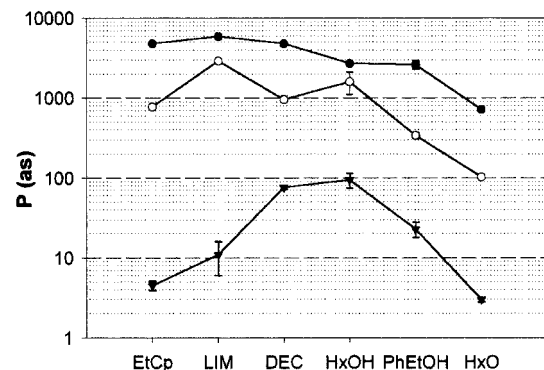1-Hexanol (HxOH), 1-hexanal (HxO), ethyl caproate (EtCp), D-limonene (LIM), *n*-decane (DEC), and 2-phenylethanol (PhEtOH) were selected as being representative of aroma components of dry-cured meat products. All liquids of reagent quality were supplied by Sigma (Teknokroma, Barcelona, Spain). Each aroma compound was tested individually.

Permeability measurements were carried out in an isostatic permeation apparatus at 23 $\pm$ 2 °C for ULDPE and ION. A test film was placed in the two-chamber permeation cell, and the upper chamber was continuously purged with a stream of the aroma vapor and nitrogen gas. The lower chamber was flushed with dry nitrogen at a flow rate of about 1 mL/min. This stream carried the permeated aroma to a gas chromatograph which was used as a detector. Permeant concentration at a vapor activity of around 0.1 was obtained by 10-fold dilution of an aroma-saturated nitrogen stream with pure nitrogen at 23 $\pm$ 2 °C (concentrations of about 300 ppb for HxOH, PhEtOH, and LIM, and 600 ppb for HxO, EtCp, and DEC). For these concentration ranges, mass transport can be considered to be concentration independent (Hernandez-Muñoz et al., 1998). An HP 5890 series II plus gas chromatograph (Hewlett-Packard, Barcelona, Spain) was used to measure aroma concentrations in both cell chambers. Additional details of the permeation cells, aroma vapor control and generation, and data treatment are described elsewhere (Debeaufort and Voilley, 1994; Gavara et al., 1996a).

Due to the low permeation rate observed through mPET, the isostatic technique was not sensitive enough for detection. mPET was therefore analyzed by the quasi-isostatic procedure. The difference between these two methods lies in how the permeated aroma is treated. In the isostatic procedure, permeated molecules are carried out of the cell to the detector where the permeation flow is monitored. In the quasi-isostatic procedure, permeated molecules are accumulated in the cell and the concentration of permeant is determined as a function of time through a sampling port. A detailed description of cells, vapor generation, experimental control, and gas chromatography has already been published (Gavara et al., 1996). Figure 1 presents an example of the data obtained from a quasi-isostatic experiment. Due to the sensitivity of the GC technique, no values were reported during the first two days of experiments. After that period, permeant concentration in-
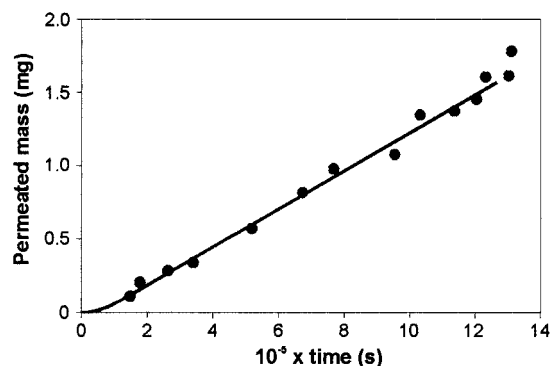
Figure 1. Data obtained through a quasi-isostatic experiment for hexanal permeating through modified polyester (mPET): (●) experimental data and (—) theoretical values obtained using solutions to Fick's laws (Gavara et al., 1996). Hexanal concentration 720 ppb.

Figure 2. Values of the permeability coefficient (P, as) of D-limonene (LIM), *n*-decane (DEC), ethyl caproate (EtCp), 2-phenylethanol (PhEtOH), 1-hexanol (HxOH), and hexanal (HxO) through (●) ultra-low-density polyethylene (ULDPE), (○) ionomer (ION), and (▼) modified polyester (mPET).

creased to detectable levels. A single experiment lasted approximately two weeks to obtain an adequate description of the permeation process.

The system is in a transient state during the initial portion of the experiment (permeation rate is a function of time) until it reaches a stationary state (permeation rate is constant). From the stationary permeation rate the value of the permeability coefficient (P) is determined. From the transient part of the experiment the kinetics of the process can be characterized through the evaluation of the diffusion coefficient. Details on the calculation procedure have been published elsewhere (Gavara et al., 1996).

To determine the effect of oil on aroma permeation through polymeric films, samples were immersed in sunflower oil for one month. Film surfaces were then thoroughly wiped with paper tissues to remove all excess oil, and permeation experiments such as those already described were conducted immediately on these films.

RESULTS AND DISCUSSION

Figure 2 presents the values of the permeability coefficient (P) obtained for the six aroma components through the three polymers under study. Values are presented in attoseconds (as), this unit being equivalent to 10^{-18} kg·m/(m^2·s·Pa) (Hernandez-Muñoz et al., 1998). As can be seen, the ULDPE is the most permeable material for all aromas. The values obtained are in agreement with values reported in the literature for similar systems: 14 800 as for LIM/HDPE (Franz, 1993), 730 as for HxO/LLDPE, and 840−4600 as for HxOH/LLDPE (Johansson and Leufven, 1994)−values
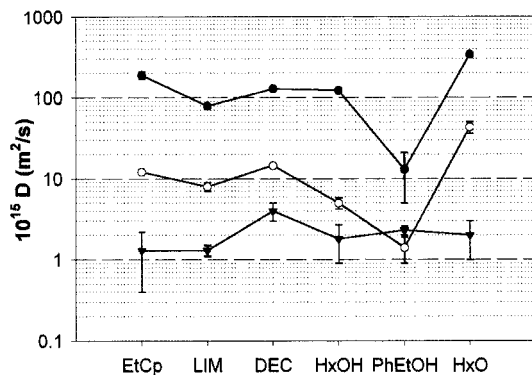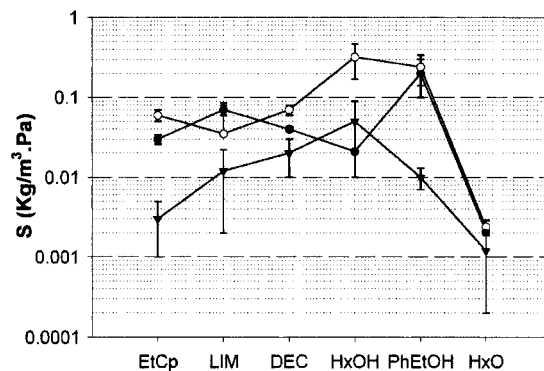
Figure 3. Values of the diffusion coefficient (*D*, m²/s) of LIM, DEC, EtCp, PhEtOH, HxOH, and HxO through (●) ULDPE, (○) ION, and (▼) mPET.

Figure 4. Values of the solubility coefficient (*S*, kg/m³·Pa) of LIM, DEC, EtCp, PhEtOH, HxOH, and HxO through (●) ULDPE, (○) ION, and (▼) mPET.

translated into attoseconds from the original units. The ionomer provides a better barrier. In terms of permeability, barrier is improved by a factor of 2 (HxO) to 10 (PhEtOH). mPET was the best barrier against aroma permeation, the aroma permeability coefficients decreasing by a factor of 100–1000 compared to ULDPE. There are no reports of permeation through mPET cast films. The reported permeability coefficients for LIM through bioriented polyester film were much lower than those through mPET (0.1 as; Apostopoulus and Winters, 1991; Franz, 1993). *P* values obtained for HxO (4 as) and HxOH (20 as) through unoriented EVOH are closer to the values presented in this paper.

With respect to the transport of various aromas through the same polymer, the permeabilities of LIM, DEC, and EtCp (the most nonpolar vapors) through ULDPE were the highest. Lesser values were obtained for HxOH and PhEtOH, and the lowest value was obtained for HxO, the aroma of smallest molecular size. A similar profile was found for the ionomer with the exception of hexanol, the permeability value of which was very high and close to that of limonene. The presence of ions in the polymer and the OH of the alcohol may promote more compatibility between them. While of a different order of magnitude, the aroma permeability profile of mPET is similar to that of ION. In this case LIM and EtCp presented permeability values lower than expected.

The permeability coefficient (*P*) is a parameter derived from the integration of Fick's laws for a permeation experiment under steady-state conditions, assuming that Henry's law applies (Hernandez-Muñoz et al., 1998). Accordingly, the value of *P* is the result of the contribution of the diffusion (*D*) and solubility (*S*) coefficients (*P = DS*). These parameters, considered to be dependent only on temperature, represent (*D*) the kinetics of the process and (*S*) the equilibrium. Therefore, it is more rigorous to discuss these results in terms of *D* and *S* than *P*, which is a mathematical artifact of both. Values of *D* and *S* were thus calculated for each aroma/film system.

Figure 3 plots the experimental values of *D*. The diffusion of the aromas studied through ULDPE and ION presented the same profiles, though the diffusion through ULDPE was approximately 1 order of magnitude higher in all cases. Values were within the same range as others previously reported: 60×10^{-15} m²/s for LIM/LLDPE (Kobayashi et al., 1995), 310×10^{-15} m²/s for HxO/LLDPE, and 120×10^{-15} m²/s for HxOH/LLDPE (Johansson and Leufven, 1994). The component

with the slowest kinetics was PhEtOH, the compound with the most rigid structure. The other aromas could be ordered in terms of their molecular weights. The heavier the molecule, the lesser the value of *D*. The values of *D* for transport through mPET were very similar for all aromas, about 2×10^{-15} m²/s (differences were within the experimental error of the quasi-isostatic technique), and below those obtained for ULDPE and ION. These values were within the range reported for the diffusion of aromas through EVOH (Johansson and Leufven, 1994).

The values of *S* obtained theoretically (*S = P/D*) are shown in Figure 4. The highest values correspond to the ION film for all aroma compounds tested. There may be morphological differences with respect to ULDPE which increase the volume available for the penetrants. Similar results were found for the partition of aromas between water and LLDPE and two ionomers (Kwapong and Hotchkiss, 1987). Solubilities in ULDPE and ION presented the same profiles with the exception of HxOH. A possible explanation for this may lie in the greater polarity of the ION due to the presence of ion groups. The high values of *S* found for PhEtOH with both ULDPE and ION might result from its low volatility (boiling point 204 °C, melting point 20 °C). The contrary applies to the low values observed for HxO. The lowest aroma solubility values were obtained in mPET with the exception of HxOH in ULDPE (already discussed in the context of the considerable differences in polarity between the alcohol and the polymer). A detailed discussion of these values is complicated due to the large errors (errors accumulate due to the calculating procedure). However, we can say that HxO is the compound with lower sorption, while the *S* differences between the rest of the aromas under study are within the range of experimental error.

mPET appears to be the best barrier against aroma permeation followed by an ionomer. mPET, the film with the lesser aroma solubility and diffusivity, is an excellent substitute for polyethylenes in aromatic food packaging. However, the substitution of PE by an ionomer may not always be such a good choice. A permeable package made with ION will reduce aroma permeation with respect to the PE alternative. However, it is important to note that the use of ION as an alternative to ULDPE in the design of multilayer high-barrier packages would not reduce the level of aroma loss. In these cases, since the high-barrier layer restricts permeation, the loss of aroma is caused by polymer

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Table 1. Values of *P*, *D*, and *S* for the Permeation of Aromas through the Films before and after Being Immersed in Oil for One Month

aroma	*P* (as)		*D* (m²/s) × 10¹⁵		*S* (kg/m³·Pa)	
	before	after	before	after	before	after
			ULDPE			
EtCp	4800 ± 100	16300 ± 600	190 ± 20	72 ± 4	0.030 ± 0.004	0.23 ± 0.02
LIM	5900 ± 400	24300 ± 500	79 ± 4	67 ± 3	0.07 ± 0.01	0.36 ± 0.01
DEC	4800 ± 100	32200 ± 200	128 ± 7	158 ± 14	0.040 ± 0.003	0.20 ± 0.02
HxOH	2700 ± 40	5400 ± 100	123 ± 3	122 ± 3	0.021 ± 0.001	0.040 ± 0.005
PhEtOH	2600 ± 300	2800 ± 300	13 ± 8	26 ± 3	0.2 ± 0.1	0.11 ± 0.02
HxO	720 ± 30	11400 ± 200	340 ± 13	275 ± 30	0.0021 ± 0.0001	0.040 ± 0.005
			ION			
EtCp	780 ± 60	2400 ± 300	12.1 ± 0.2	12 ± 3	0.06 ± 0.01	0.19 ± 0.07
LIM	2920 ± 80	5200 ± 300	8 ± 1	9 ± 1	0.35 ± 0.05	0.6 ± 0.1
DEC	960 ± 90	4400 ± 300	14.5 ± 0.5	25 ± 5	0.07 ± 0.01	0.17 ± 0.05
HxOH	1600 ± 500	1100 ± 300	5.0 ± 0.8	3 ± 1	0.32 ± 0.15	0.37 ± 0.19
PhEtOH	340 ± 30	460 ± 30	1.4 ± 0.5	1.7 ± 0.5	0.24 ± 0.10	0.27 ± 0.09
HxO	103 ± 6	270 ± 10	43 ± 7	30 ± 5	0.0024 ± 0.0005	0.01 ± 0.002
			MPET			
EtCp	4.5 ± 0.6	14.0 ± 0.6	1.3 ± 0.9	2.7 ± 0.2	0.003 ± 0.002	0.010 ± 0.005
LIM	11 ± 5	90 ± 40	1.3 ± 0.2	3.5 ± 0.5	0.01 ± 0.01	0.03 ± 0.02
DEC	76 ± 3	120 ± 60	4.0 ± 1.0	2 ± 1	0.02 ± 0.01	0.06 ± 0.04
HxOH	95 ± 20	120 ± 50	1.8 ± 0.9	1.5 ± 0.5	0.05 ± 0.04	0.08 ± 0.06
PhEtOH	23 ± 5	20 ± 1	2.3 ± 0.3	2.7 ± 0.5	0.010 ± 0.003	0.010 ± 0.002
HxO	3.0 ± 0.2	8 ± 2	2 ± 1	3.0 ± 0.9	0.001 ± 0.001	0.003 ± 0.001

retention, and therefore, the higher solubilities of aromas in ION would cause an increase in flavor scalping.

As pointed out in the Introduction, the transport of other food components present in large amounts such as water or fats may alter the permeation of gases and vapors. The mass transport of aromas through the three films under study was also analyzed after exposure of the films to sunflower oil. The permeation results were characterized in terms of *P*, *D*, and *S* and are included in Table 1 (average and standard deviation of three experiments). Since the polymer matrixes would have sorbed oil, the most significant effects were expected on *S*.

When a polymeric matrix sorbs a compound, the molecules are adsorbed or absorbed in the free volume ("holes") which is always present in the amorphous regions. This uptake may fill these empty spaces and, sometimes, may relax the polymer, reducing the intercatenary forces and even promoting polymer swelling. Permeation experiments on the six organic compounds were carried out on films previously immersed in oil. There are two possible effects of oil in aroma mass transport: (1) the oil and the new penetrant compete for the same sites, reducing the solubility of the aromas since many sites are already occupied, and (2) the oil swells the polymer, opening the structure and increasing polymer free volume. As Table 1 shows, the solubility values for EtCp, LIM, DEC, and HxO increased in all three polymers. This effect was greater in ULDPE. These higher values may indicate that some polymer swelling might have occurred. However, the sorbed oil effect on *S* was not as large for HxOH and PhEtOH. The solubility of the latter was even reduced by the presence of oil in ULDPE. This difference in behavior can be interpreted as a question of compatibility. In a previous paper, the sorption of water was found to increase the solubility of polar substances and reduce that of nonpolar compounds (Aucejo et al., 1998). HxOH and PhEtOh are polar substances while both the polymers and the sorbed oil are nonpolar, and consequently the presence of oil may reduce the already low compatibility between these aromas and the polymer matrixes.

Diffusion coefficient values are also presented in Table 1. As can be seen, no clear effect of oil on the kinetics of aroma mass transport was found. One might have expected that polymer swelling increased the free volume and consequently the kinetics of permeation. However, the portion of matrix volume not filled by the polymer is occupied by long oil molecules, and therefore, the anticipated effect is counteracted.

Finally, the effect of oil on permeability values is the combination of oil effects on *D* and *S*. Since *D* was barely affected, *P* values reflected the effects on *S*. Nonpolar penetrants greatly increased their permeation rates through oiled films while polar penetrants demonstrated little or no effect of oil presence. This effect may be very important in the packaging of fatty foods if permeability values to aromas through films (not contaminated by food) are used in the design of the package structure. The significant permeation increment of nonpolar aroma components caused by fat sorption may promote a flavor imbalance, which may result in shortened shelf life.

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